

Solar-driven photocatalysis for recycling and upcycling plastics

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ABSTRACT

The widespread use of plastics in modern societies generates huge amounts of plastic waste. With a view toward sustainability, researchers are now seeking strategies for recycling and upcycling plastic waste to valuable products. There is currently a significant amount of research on thermal catalytic recycling of plastics. These studies are mostly limited by high energy input, and the economic efficiency of the reaction process is not ideal. Photocatalysis and photothermal catalysis show superiority in terms of energy compared to traditional thermal catalysis. Recent researches about photocatalysis and photothermal catalysis to achieve chemical recycling and upcycling of plastics are reviewed, especially for the concept and application of three types of photothermal catalytic processes. Considering the most important efficiency, energy, and separation issues in plastic recycling, photothermal catalysis has a huge potential in the future field of plastic chemical recycling and upcycling.

1. Introduction

The use of plastics brings great convenience to modern human life. As a type of man-made materials, plastics have the advantages of low cost, durability, light weight and wide applicability [1], resulting in the continuous growth of plastics demand and production in the past decades. Nowadays, more than 300 million tons of plastics are manufactured each year [2], and only 17% of plastic wastes are recycled [3]. Most of plastic products are made of non-degradable plastics, such as polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET), and polyurethane (PUR). It would take hundreds of years for these non-degradable plastics to degrade in the natural environment. These plastics have caused serious environmental pollution and ecological crisis [4–6]. Even the so-called degradable plastics, such as polylactic acid (PLA), and polycarbonate (PC), require special conditions (light irradiation, microorganism, enzyme etc.) to degrade them eventually into water and greenhouse gas carbon dioxide [7–11]. To attack the growing eco-crisis and recycle the carbon source in plastic wastes, it is urgent to develop efficient technologies to degrade and upcycle the plastics.

In the chemical structure of plastics, the structural units are usually connected by stable C-C or C-O bonds (Fig. 1). Recycling technologies of

plastic wastes include mechanical recycling and chemical recycling. Mechanical recycling consists of physical processes such as grinding, extruding, compounding, and pelletizing without changing the chemical composition. This strategy is not applicable to the recycling of a large amount of actual plastic wastes, due to its special requirements in the purity and mechanical properties of plastic wastes [12]. Chemical recycling has great potentials, which aims to chemically convert plastic wastes into their monomers or other small-molecule chemicals. A number of chemical processes have been developed to recycle plastic wastes, such as pyrolysis, solvolysis, hydrogenolysis, reforming, oxidation and hybrid process [3,12–17]. However, plastics have the properties of high molecular weight and poor solubility, making it difficult to effectively contact and react with other molecules, thus possessing high chemical stability.

Polyolefins (including LDPE, HDPE and PP) are the most important category among all the plastics, which account for more than half of the total plastic production and are applied in various fields such as electrical insulators, toys, bottles, packaging, constituent of devices [12]. The stable and similar C-C bonds in the chemical structure of polyolefins bring huge difficulty for chemical recycling and upcycling. Mixed hydrocarbon products can be obtained through pyrolysis [18–22] or hydrogenolysis [23–28] processes with high energy input, but such

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processes are economically inefficient. PS is another hydrocarbon plastic with similar properties and applications with polyolefins. Similarly, PS can be converted into mixed aromatic hydrocarbons through high-energy input pyrolysis [29–31] and hydrogenolysis [32–34] processes. Recently, a number of works reported that PS can be selectively oxidized to benzoic acid by oxygen with photocatalysis systems [35–38]. However, the efficiency of these photocatalytic processes is generally low. PVC is a notorious type of polymer for chemical recycling and upcycling. The high content of chlorine in PVC is easily removed in the form of hydrogen chloride (HCl) during various recycling processes, which lead to the corrosion of reactor and the poisoning of catalysts. One strategy for treating chlorine containing waste plastics is to add excess alkali to the reaction system to absorb the HCl produced [39]. Another solution is to absorb and store the generated HCl and use it for other reaction processes that require chlorine [40]. PET and PUR are the most used polymer except for the polymers by the C-C bond addition polymerization mentioned before. The major recycling method for these two plastics is to obtain monomers and oligomers through solvent hydrolysis, such as hydrolysis [41–43], alcoholysis [44–46], acidolysis [47], and ammonolysis [48,49]. Due to the relatively simple chemical structure and high recycling ratio of PET (most plastic bottles), chemical recycling of PET is relatively mature, while the researches about chemical recycling and upcycling of PUR is less [50–52]. The recycling of degradable plastics such as PLA and PC is relatively simple and can be performed under mild conditions. However, these types of plastics have low production and low pollution, and related research has received less attention than non-degradable plastics. In summary, recycling and upcycling of polyolefins (PE, PP) require high energy input and are difficult to get satisfied product yield and distribution, which need more research effort in the future. Research of other polymers with lower difficulty of chemical recycling should focus on other practical issues,

such as mild conditions, higher conversion efficiency, economy of process, tolerance of impurities and multiple components. Thus, it is critically important to develop green and sustainable strategies to recycle or upcycle plastic wastes.

In recent years, solar energy has been widely applied to drive various types of chemical reactions, including chemical recycling and upcycling of plastic wastes [53–56] through photocatalysis and photothermal catalysis. Photo-induced cleavage of chemical bonds (e.g., C-C, C-O or C-N) in plastics can be achieved. This provides an alternative solution to plastics recycling, by avoiding high consumption of fossil fuels. With the assistance of photons, substrates can be activated into radical species or react with other radicals. This photocatalytic reaction mechanism can be effective for the plastic substrates with high thermal stability. Meanwhile, the active radical species may solve the problems of contact between plastic substrates and heterogeneous catalyst to improve reaction efficiency. Moreover, the photo-induced catalytic mechanisms (e.g., different from that of thermal catalysis) make it possible to achieve unique product selectivity in some reactions, which is difficult to be achieved by thermal catalytic mechanisms. Quite a few reviews summarized the recent progress in chemical recycling and upcycling of plastic wastes. But few of them focused on the difference and the development of photocatalysis and photothermal catalysis. Herein, we provide a critical review of photo-induced recycling or upcycling of plastic wastes, demonstrating the characteristics of three categories photons-induced catalysis, and potential challenges of utilizing solar energy in real applications.

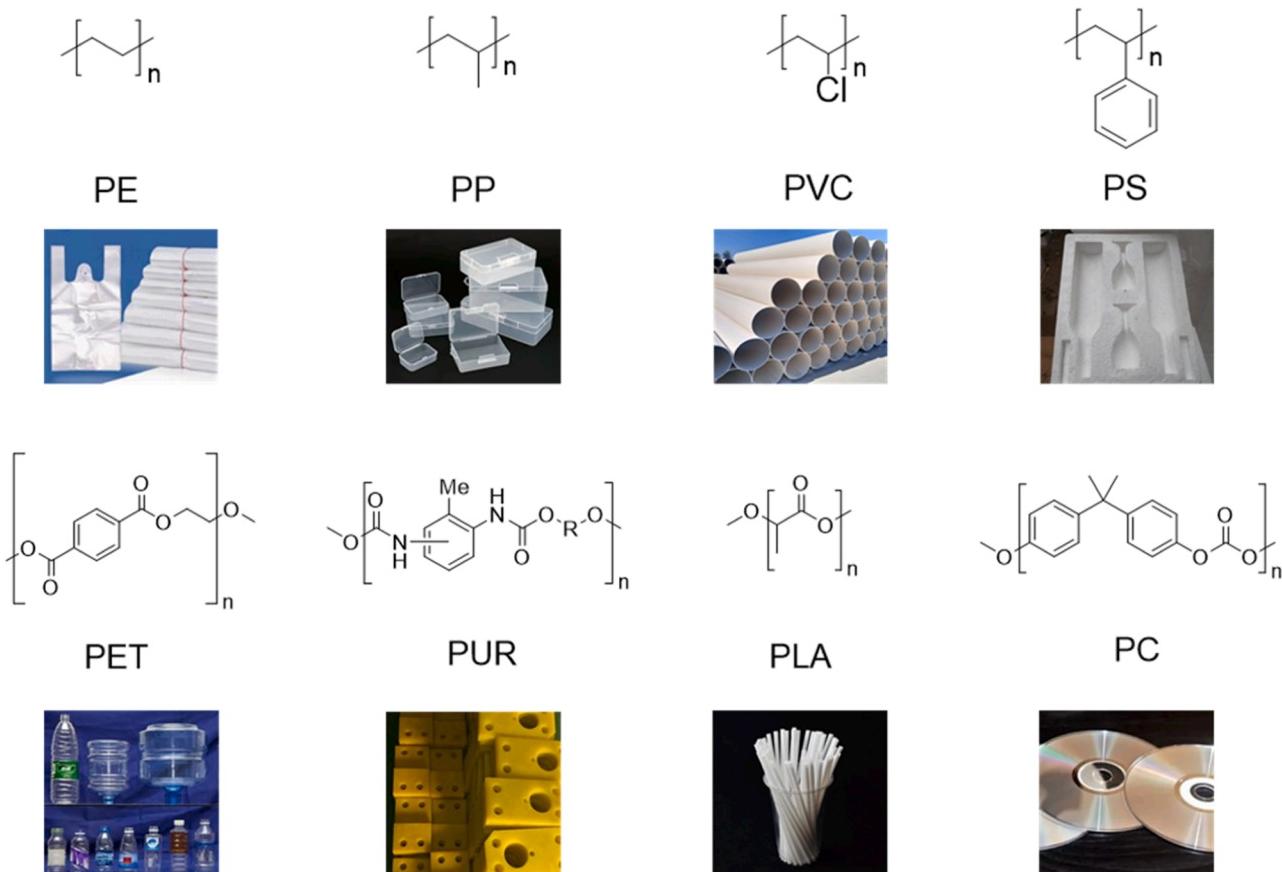


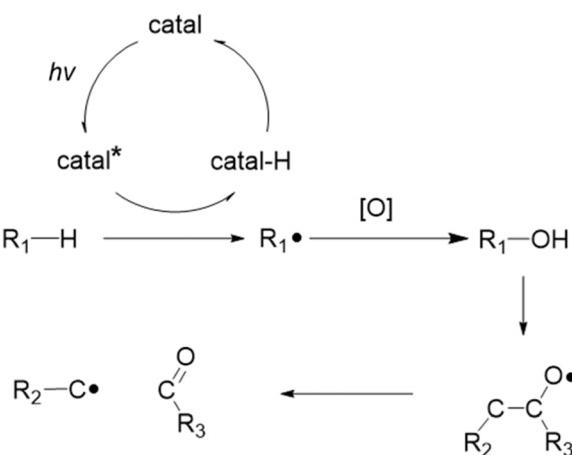
Fig. 1. The chemical structure of common plastics and their typical plastic products.

2. Photocatalysis conversion of plastics

2.1. Fundamental mechanism of photocatalysis in plastics recycling and upcycling

Photocatalytic plastics depolymerization can take place in both heterogeneous semiconductor and solution catalytic systems. In heterogeneous semiconductor catalytic system, it is generally accepted that the reaction involves three fundamental steps on a semiconductor photocatalyst [57–59]: 1) photon absorption and formation of electron–hole pairs; 2) separation and migration of photogenerated electrons and holes; 3) surface redox reactions initiated by the photogenerated electrons and holes (Scheme 1). The entire reaction process may be viewed as an oxidative half reaction and a reductive half reaction. In the oxidative half reaction, plastics undergo oxidation to generate CO_2 or other carbonaceous chemicals. The reduction half reaction may include the reduction of proton in water to produce hydrogen, or the consumption of oxidants such as oxygen. Apart from direct reaction between reactant molecules and electron-hole pairs to yield products, the photo-induced electrons and holes are also involved in the generation of reactive oxygen species (ROS), such as hydroxyl radical ($\bullet\text{OH}$) [60], singlet oxygen ($^1\text{O}_2$) [38] and superoxide anion ($\bullet\text{O}_2^-$) [37,60]. ROS is more likely to act on the plastics and leads to bond cleavage than direct reaction between plastic reactants and electron-hole pairs, because the reaction of ROS has the advantage of diffusion than the heterogeneous reaction on the surface of catalyst. The redox ability of photogenerated electrons and holes is determined by the intrinsic properties of semiconductors. The optimization strategies for heterogeneous catalytic systems include controlling band structures and promoting the separation (or preventing the recombination) of electron-hole pairs, through doping and structural control of catalysts.

Compared with heterogeneous semiconductor photocatalysis, solution photocatalysis has fewer applications in plastic recycling and upcycling. At present, relevant examples are mostly limited to the photocatalytic oxidation of PS [36,61]. A mechanism of radical oxidation and C-C bond scission can be involved (Scheme 2). The photocatalyst is excited under light irradiation, and then obtains a hydrogen atom from the C-H bond in the substrate directly through hydrogen atom transfer (HAT), or induces the formation of ROS which subsequently react with C-H bond, leading to a carbon radical. Subsequently, a C-O bond is formed in the presence of oxidants, resulting in the formation $\text{C}-\text{C}-\text{O}\bullet$ radical after another HAT process. Then, the $\text{C}-\text{C}-\text{O}\bullet$ radical undergoes β -scission step to form shorter chains, reducing the molecular weight of polymer substrate and eventually forming small-molecule products. It is noticed that the bond scission process by radicals may not exist only in homogeneous photocatalysis systems. Active radicals and similar processes have been observed in some heterogeneous photocatalytic systems [37,60]. The activity of radicals in such reactions is affected by a few of factors such as light source, temperature, atmosphere, solvent, and acid/base property.

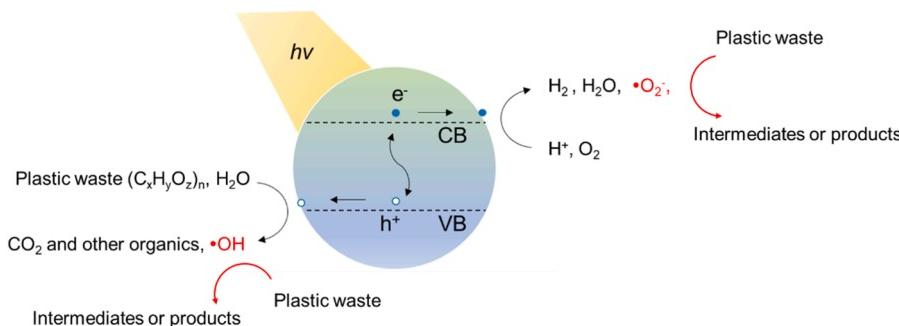


Scheme 2. Mechanism of photocatalytic oxidative conversion of plastics in a solution catalytic system.

2.2. Photocatalysis of plastics

The simplest example of photocatalytic conversion of plastics is the photo-induced degradation of plastics. Relevant publications can be traced back to 1950s [62–64]. In those works of early years, it was found that different types of plastics degraded under light irradiation and high temperature. Some small-molecule products could be detected during the degradation process, and the chemical changes of polymers were detected by infrared spectroscopy. Nowadays, many photocatalytic systems have been developed to degrade different types of plastics, including PE [65–69], PP [70–73], PS [74–77], and PVC [78–82]. Researchers have employed different strategies, such as surface structure modification [83], formation of new heterojunctions [84], and the design of multicomponent structures [85], to maximize the efficiency of catalyst. Although these photodegradation methods have advantages such as less release of toxic gases compared to incineration, they lose the chemical energy released during the combustion. In addition, the photodegradation products CO_2 and H_2O are not valuable. Most of these works about plastic degradation do not consider the value of degradation product and the economy of degradation reaction. In general, such photocatalytic degradation systems are not an ideal or low-carbon strategy for plastics treatment.

Another photocatalytic strategy applies the plastics as sacrificial agent for the oxidation half reaction and uses the reduction half reaction to produce value-added chemicals (mainly hydrogen). This strategy was first applied in 1981 by Tomoji and Tadayoshi [86]. The hydrogen production was observed by mass-spectrometer when PVC and water were irradiated by xenon lamp in the presence of TiO_2 catalyst. Some recent representative works of photocatalytic plastic recycling and upcycling have been listed in Table 1. In recent years, Reisner and co-workers designed a CdS/CdO_x photocatalytic system to produce



Scheme 1. Mechanism of photocatalysis of plastic conversion with a heterogeneous semiconductor catalyst.

Table 1

Comparison of recent works about photocatalysis and photothermal catalysis for plastic recycling and upcycling.

Catalyst	Plastic and reaction	Mechanism of catalysis	Light source	Main product	Temperature	Gas and pressure	Solvent	Yield of product ^a (%)	Catalytic activity ^b (mmol g _{catal} ⁻¹ h ⁻¹)	Reactor	Active species
CdS/CdO _x (quantum dots) [87]	PLA, PET, PUR (water reforming)	photocatalysis	simulated sunlight	H ₂	25 °C	1 bar N ₂	aqueous NaOH	38.8 (PLA), 16.6 (PET), 22.5 (PUR)	64.3 (PLA), 3.42 (PET), 0.85 (PUR)	batch reactor	unspecified
CN _x Ni ₂ P [88]	PET, PLA (water reforming)	photocatalysis	simulated sunlight	H ₂	25 °C	1 bar N ₂	aqueous KOH	24.5 (PET), 6.7 (PLA)	0.0257 (PET), 0.0557 (PLA)	batch reactor	e ⁻ ·h ⁺ , ·OH
Nb ₂ O ₅ [60]	PE, PP, PVC (water reforming)	photocatalysis	Xe lamp	acetic acid, CO ₂	25 °C	1 bar air	water	Not provided	0.525 (CO ₂), 0.0008 (acetic acid)	batch reactor	e ⁻ ·h ⁺ , ·OH, ·O ₂ [·]
Co-Ga ₂ O ₃ [91]	PE, PP (water reforming)	photocatalysis	simulated sunlight	CO, H ₂ , CO ₂	25 °C	1 bar air	water	Not provided	0.6478 (H ₂), 0.1583 (CO)	closed glass gas-circulation system	e ⁻ ·h ⁺ , ·OH, ·O ₂ [·]
V(O)(acac) ₂ [105]	PE, PP, PVC, etc (aerobic oxidation)	photocatalysis	white LED	formic acid	25 °C	1 bar O ₂	acetonitrile	0.6 (PE)	0.025 (PE)	batch reactor	· OH, ·O ₂ [·]
fluorenone, H ₂ SO ₄ [92]	PS (aerobic oxidation)	photocatalysis	blue LED	benzoic acid	50 °C	1 bar O ₂	ethyl acetate	30	0.520	batch reactor	photoexcited HAT organic catalysts
FeCl ₂ [61]	PS (aerobic oxidation)	photocatalysis	400 nm LED	benzoic acid	25 °C	1 bar O ₂	DCM/acetonitrile	65	3.89	batch reactor	Fe(III), ¹ O ₂
pTsOH [38]	PS (aerobic oxidation)	photocatalysis	405 nm LED	formic acid, benzoic acid	25 °C	1 bar O ₂	benzene/acetonitrile	50	5.19 (formic acid), 3.87 (benzoic acid)	batch reactor	¹ O ₂ , ·OR, ·R
FeCl ₃ [35]	PS (aerobic oxidation)	photocatalysis	white LED	benzoic acid	25 °C	ambient airflow	acetone	11.3	0.543	flow system	· Cl
FeCl ₃ +TBACl [36]	PS (aerobic oxidation)	photocatalysis	390 nm LED	benzoic acid	25 °C	1 bar O ₂	acetonitrile	67	0.344	batch reactor	· Cl/·OR, ·O ₂ [·]
g-C ₃ N ₄ [37]	PS (aerobic oxidation)	thermal-assisted photocatalysis	Xenon lamp	benzoic acid	150 °C	10 bar O ₂	acetonitrile	58	0.082	batch reactor / circulatory liquid system	e ⁻ ·h ⁺ , ·O ₂ [·]
CNT-PDA [102]	PET (glycolysis)	light-driven thermal catalysis	simulated sunlight	BHET	180 °C	air	glycol	51	5.3	batch reactor	unspecified
Co SSA-CNT@PDA [106]	PET (glycolysis)	light-driven thermal catalysis	simulated sunlight	BHET	180 °C	air	glycol	83	48	batch reactor	unspecified
TiO ₂ -DEG [107]	PET (glycolysis)	photothermal synergistic catalysis	simulated sunlight	BHET	190 °C	air	glycol	85	220	batch reactor	e ⁻ ·h ⁺ , Ti ³⁺ , O _v
Ni-TiO ₂ -Al ₂ O ₃ [103]	LDPE (pyrolysis)	photothermal synergistic catalysis	simulated sunlight	C8-C16 jet fuel	500 °C	N ₂ flow	solvent free	39	56 *	fixed bed reactor	unspecified
Ru-TiO ₂ [104]	LDPE (hydrocracking)	photothermal synergistic catalysis	simulated sunlight	C5-C21 liquid fuel	220 °C	30 bar H ₂ /N ₂	solvent free	86	184 *	batch reactor	unspecified

^a Yield = conversion of plastics × selectivity of main product in all detected product.^b It is hard to calculate the molar amount of the product in works with mixed hydrocarbon products. In this type of work, the number of moles in the rate unit represent the number of moles of carbon, denoted by *.

hydrogen [87] from polyesters (PET, PLA and PUR). Despite some high initial activities, the overall conversion remained below 40% for all polymers. The authors claimed that the incomplete mineralization of plastic substrate prevented the discharge of a greenhouse gas and allows for the beneficial accumulation of high-value products in solution. In a follow-up work of Reisner group, a cheap and nontoxic nitride/nickel phosphide ($\text{CN}_x/\text{Ni}_2\text{P}$) photocatalyst was designed [88], which showed similar performance to the Cd-based catalysts. They also designed a scalable photocatalyst panel to overcome several practical scaling challenges [89]. Subsequently, a photocatalyst was developed for hydrogen production from the polyester and water reforming by Zhang and co-workers [90]. However, none of these works were able to fully reform the plastic waste to produce H_2 . The current limits of low conversion of plastic substrate and complex liquid products make it difficult to scale-up the photocatalysis process for real application. In addition, the produced hydrogen cannot be used directly due to the presence of CO_2 product. Such photocatalytic reforming systems cannot be applied to polyolefins. Hence, it is in demand to develop reforming catalytic systems for a wider range of plastic wastes that can further convert CO_2 and H_2 to hydrocarbons or other value-added chemicals. Another drawback of these early works focused more on the study of reaction phenomena and did not pay attention to mechanism information such as reaction pathways, active intermediates.

Recently, Xie et al. developed a bifunctional Nb_2O_5 catalyst to

photodegrade plastic wastes into CO_2 , followed by the formation of C2 chemicals [60] (Fig. 2a and b). The Nb_2O_5 catalyst has proper band structure to generate oxidative $\bullet\text{OH}$ and $\bullet\text{O}_2$ to break the C-C bonds and to provide electrons for CO_2 photoreduction through C-C coupling. The reaction was carried out in an oxidizing atmosphere (air) and had a high plastic degradation efficiency. Meanwhile, the rate of CO_2 reductive coupling to C2 production was limited, which was only about 1% of the rate of CO_2 production. It is confirmed by Electron Paramagnetic Resonance (ESR) that reactive $\bullet\text{OH}$ and $\bullet\text{O}_2$ are generated under reaction conditions when the catalyst is irradiated with light (Fig. 2c). Through in-situ Fourier transformed Infrared (FTIR) experiment (Fig. 2d), the authors confirmed the formation of $\bullet\text{COOH}$ intermediates during the PE photoconversion process. Combined with other isotope labeling experiments, it has been confirmed that CO_2 originates from the oxidation of plastics. Although this process is not efficient for C2 production, it provides an example of converting stubborn polyolefins into chemicals by photocatalysis. In their follow-up work [91] (Fig. 2e), a $\text{Co}-\text{Ga}_2\text{O}_3$ nanosheet photocatalyst was designed to convert plastics into syngas. Similar infrared spectroscopy experiments have also been used to confirm the CO generation pathway (Fig. 2f). However, most of CO_2 (about 2/3 of total carbon) generated from oxidation of plastics was not converted to CO.

For some plastics with special chemical structures, it may not be wise to completely degrade them into CO_2 (and then to other chemicals). The

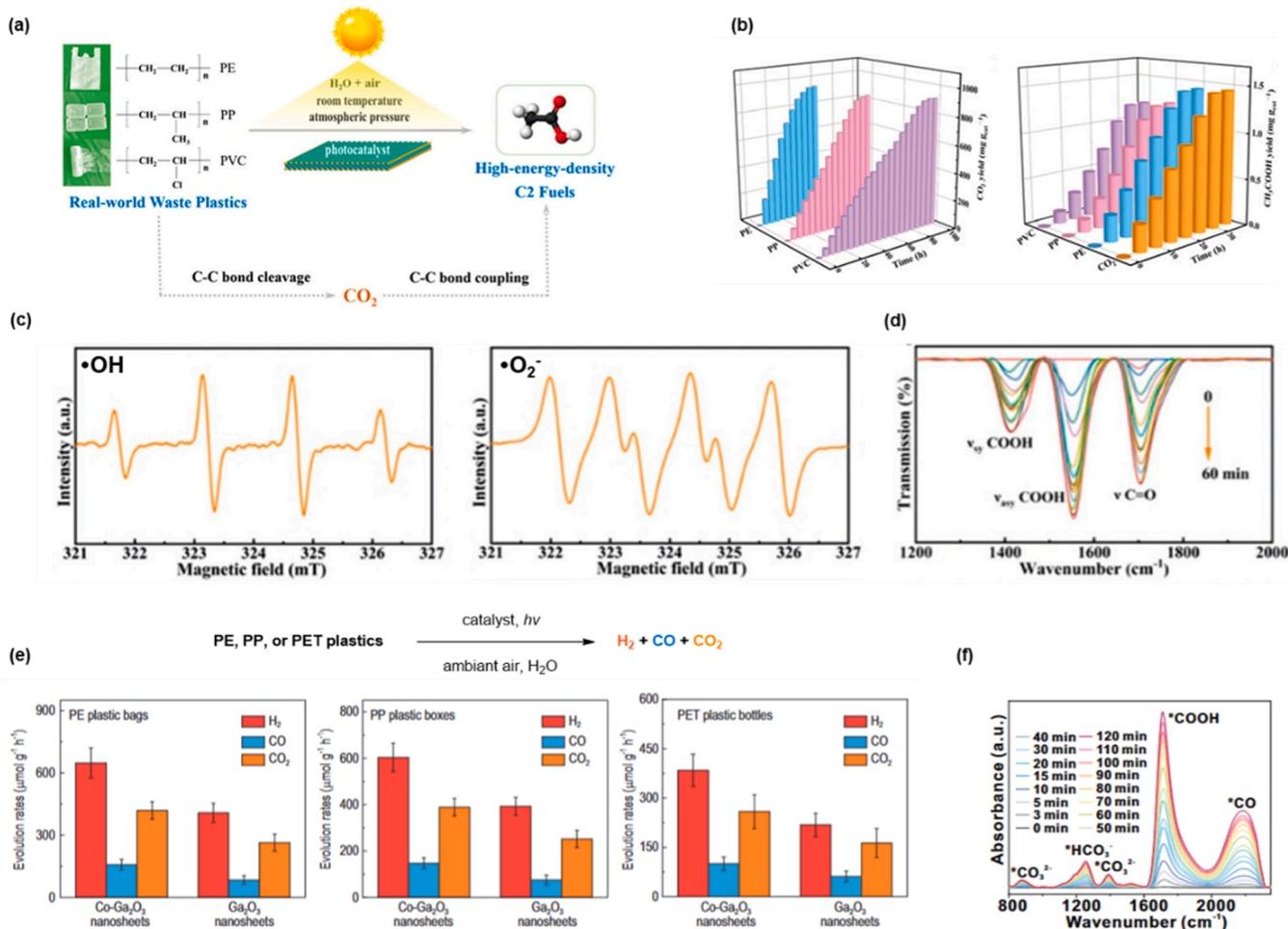


Fig. 2. Photocatalytic conversion of PE, PP and PVC into value-added chemicals [60,91]. (a) Schematic illustration for converting various waste plastics into C2 chemicals by a two-step pathway in a simulated natural environment. (b) The yield of CO_2 (left) and acetic acid (right) during the photoconversion of pure PE, PP, and PVC over the Nb_2O_5 atomic layers. (c) Identification of hydroxyl radical ($\bullet\text{OH}$), superoxide group ($\bullet\text{O}_2^-$) by EPR. (d) In-situ FTIR spectra of CO_2 photoreduction to acetic acid process. (e) Evolution of H_2 , CO, and CO_2 photo-reduced from non-recyclable plastics by Ga_2O_3 catalyst. (f) In-situ FTIR spectra of CO_2 photoreduction to CO with $\text{Co}-\text{Ga}_2\text{O}_3$ catalyst.

photocatalytic system may selectively activate specific chemical bonds in their structure, to generate certain products. PS is featured with stable benzene rings in structure, and it is possible to selectively depolymerize the PS chain without destroying benzene rings. Zeng and co-workers first used FeCl_3 as catalyst and oxygen as an oxidant, to oxidize PS to benzoic acid in a yield of 67% [36]. After that, several research groups developed other catalytic systems, including FeCl_3 [35,61], acid catalyst [38], HAT C-H oxidation catalyst [92] and heterogenous catalyst [37], for the photocatalytic oxidation of PS to benzoic acid. The conversion mechanisms among these works are similar (Fig. 3a). Under the condition of photocatalysis, the C-H in aliphatic carbon chain of PS is oxidized

to produce radicals and oxygen-containing functional groups. Then, small-molecule products are formed gradually by a radical oxidation mechanism. The photocatalysis mechanism was investigated with several different aspects. Reisner et al. [92] found a linear relationship between fluorescence signal attenuation of photocatalyst and PS concentration (Fig. 3b, Stern-Volmer fluorescence quenching experiments), suggesting that the excited state of the photocatalyst was quenched by PS as reaction was conducted. Hu et al. [61] used TEMPO to capture oxidation intermediate in the reaction of model compound, and demonstrated that this intermediate and substrate exhibited similar reaction behaviors (Fig. 3c). Xiao et al. [38] employed EPR to confirm the

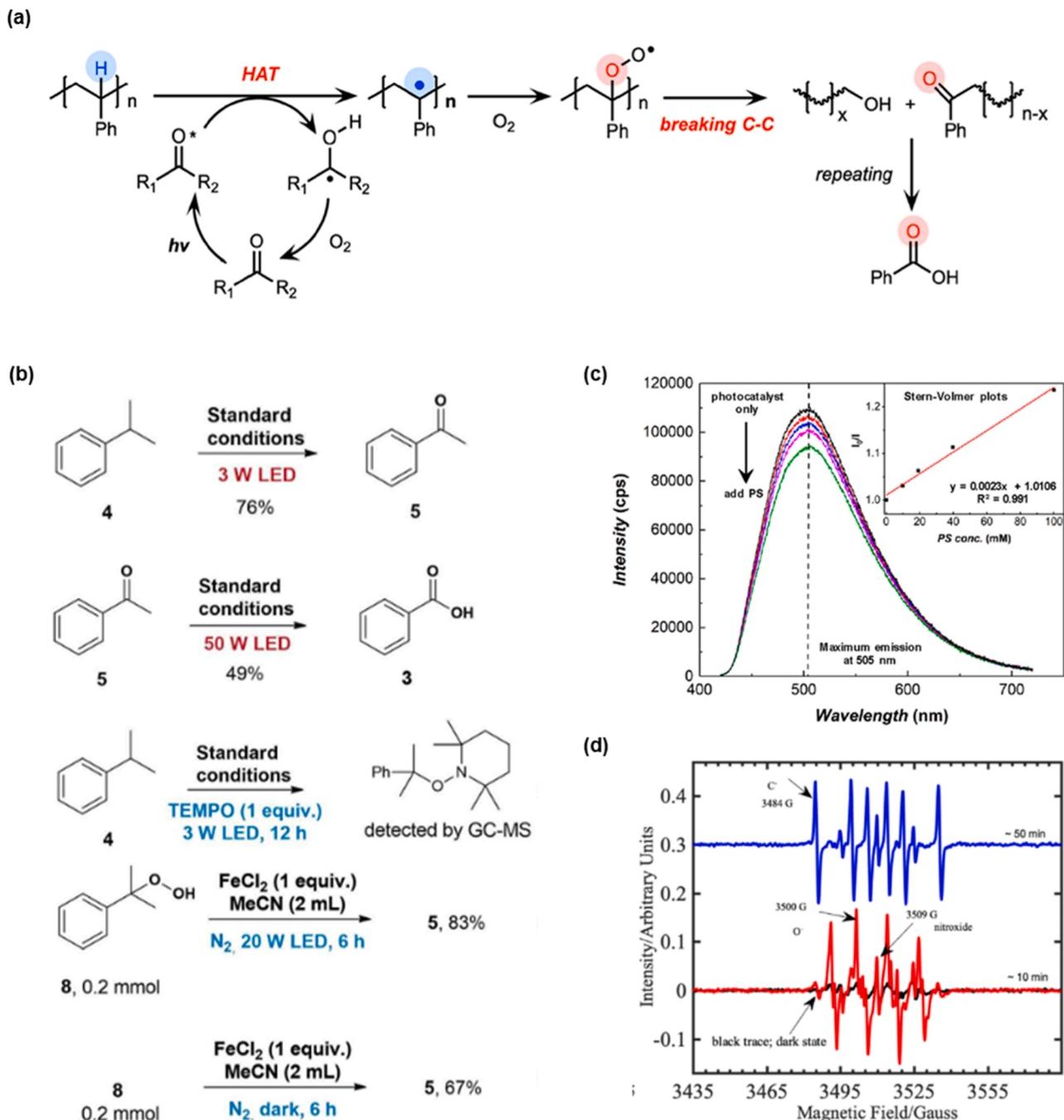


Fig. 3. Photocatalytic conversion of PS. (a) Photocatalytic deconstruction of PS to produce benzoic acid via a HAT route [92]. (b) Substrate performance and investigation of intermediate using cumene as model molecule [61]. (c) Fluorescence spectra of the photocatalyst before and after adding PS into the solution [92]. (d) EPR spectra measured after 10 min (red) and 50 min (blue) irradiation in aerobic oxidation of PS. Simulation showed the existence of DMPO-OR and DMPO-R [38].

formation of singlet ^1O_2 under irradiation, and demonstrate the generation of $\bullet\text{OR}$ radicals in the beginning of reaction and the subsequent formation of $\bullet\text{R}$ radicals *in situ* experiments (Fig. 3d). In addition to oxidation reactions, Liu et al. found that PS can decompose into arenes in benzene solution in the presence of AlCl_3 under ultraviolet light [93]. The arene intermediates could lead to the formation of diphenylmethane. In this work, the specific mechanism of light was not thoroughly studied.

Although we have highlighted some photocatalysis research works as possible solutions of chemical recycling and upcycling of plastics, these processes are still far from practical application. Cost and efficiency are the main factors that limit the practical application of photocatalysis. Though some photocatalytic processes are more advantageous than thermal catalytic processes in terms of reaction route and energy input, the reaction efficiency of most photocatalytic processes is generally rather low. Active radical species or separated electron-hole pairs in the photocatalytic reaction are not easy to produce in large quantities and not stable prior to the effective reactions. Besides, the photocatalytic process can only take place on a nearly two-dimensional illuminated surface. Reactors for such reactions are not easy to scale up. All of these issues are challenges for future applications in photocatalytic plastics recycling and upcycling.

2.3. From photocatalysis to photothermal catalysis

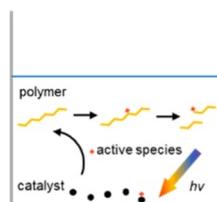
Traditional photocatalysis usually uses thermostatic devices to eliminate the interference of thermal effect, especially for reactions with the requirement of high selectivity [94,95]. However, the main problem in the plastics recycling or upcycling process is not selectivity, but the activation of plastic substrates with high chemical stability. Therefore, the introduction of thermal effect in the process of photocatalytic plastic conversion is likely to have a positive effect. Naturally, the solar energy irradiated on the semiconductor catalyst will not be completely used for the electron-hole separation process. Some solar energy is transformed to thermal energy by three mechanisms: thermal vibration, non-radiative relaxation, and plasmonic heating [95,96]. Thermal vibration mechanism includes the excitation of electron from HOMO to LUMO when molecules are irradiated and the photoexcited electrons relax back to the ground state to generate heat. Thermal vibration

mechanism usually occurs in carbonaceous and some polymeric materials [97,98]. Non-radiative relaxation mechanism occurs in semiconductor materials [99]. After the electrons and holes in semiconductor are separated under irradiation, the excited electrons can relax to lower energy states to release energy by radiative or non-radiative relaxation. Radiative relaxation release energy in the form of photon emission while non-radiative relaxation release heat via lattice vibrations. Plasmonic heating happens when the electromagnetic field of light matches the resonant frequency of conduction band electrons in the surface of conducting materials (especially metal nanoparticles) to generate high concentration of energetic (hot) electrons, which is also referred to plasmon. The plasmon decay via the non-radiative pathway can couple to phonon modes by electron-phonon scattering and thereby heat up the lattice [100,101]. Thermal energy may promote reaction in many ways, which change the original photocatalysis into photothermal catalysis. Photothermal catalysis, the reactions containing the essential factors of light, heat, and catalytic conversion, can be divided into three categories according to their reaction pathways and the roles of light and heat in the reaction: thermal-assisted photocatalysis, light-driven thermal catalysis, and photothermal synergistic catalysis [53,95] (Scheme 3).

Thermal-assisted photocatalysis mainly follows photo-driven mechanism by photogenerated electron-hole pairs or photoinduced ROS. In this catalytic system, thermal energy can facilitate mass transfer, adsorption and desorption, and provide the activation energy of reaction. The feature of this type of photothermal catalysis is that the catalyst shows no thermal catalysis performances. The work of Ma et al. on heterogeneous catalytic oxidation of polystyrene [37] is an example (Fig. 4). The g-C₃N₄ catalyst showed little catalytic activity under the 150 °C heating condition without light irradiation (< 5% conversion for 40 h). While under light irradiation and 150 °C, the conversion of PS substrate reached over 50% in 10 h. The reaction rate increased significantly with the increase of temperature (Fig. 4a). By analyzing the FTIR spectra of PS polymer under different reaction conditions and time (Fig. 4b), it was found that the oxidation of PS in the presence or absence of light can produce oxygen-containing functional groups in the polymer structure quickly, even not much product was produced. In the presence of catalyst and light irradiation, $\bullet\text{O}_2$ reactive species can be detected (Fig. 3c) and the reaction are proceeded. Therefore, the authors

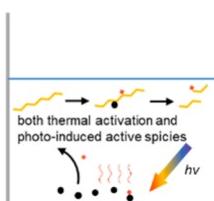
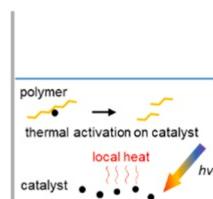
Thermal-assisted photocatalysis

- Photo-induced generation of active species (e^-h^+ , ROS)
- No reaction occurs without light irradiation
- Optimized reaction performance at high temperature



Light-driven thermal catalysis

- Thermal activation of reactant, no photo-induced active species involved
- Similar reaction performance at high temperature without light
- Photothermal conversion leads to localized hotspots around catalyst



Photothermal synergistic catalysis

- Both thermal activation of reactant and photo-induced generation of active species (e^-h^+ , ROS) are involved
- Reaction occurs when light irradiation or high temperature is absent, but the performance is poor
- Synergistic effect of thermal catalysis and photocatalysis results in excellent reaction performance

Scheme 3. Mechanism comparison of three types of photothermal catalysis.

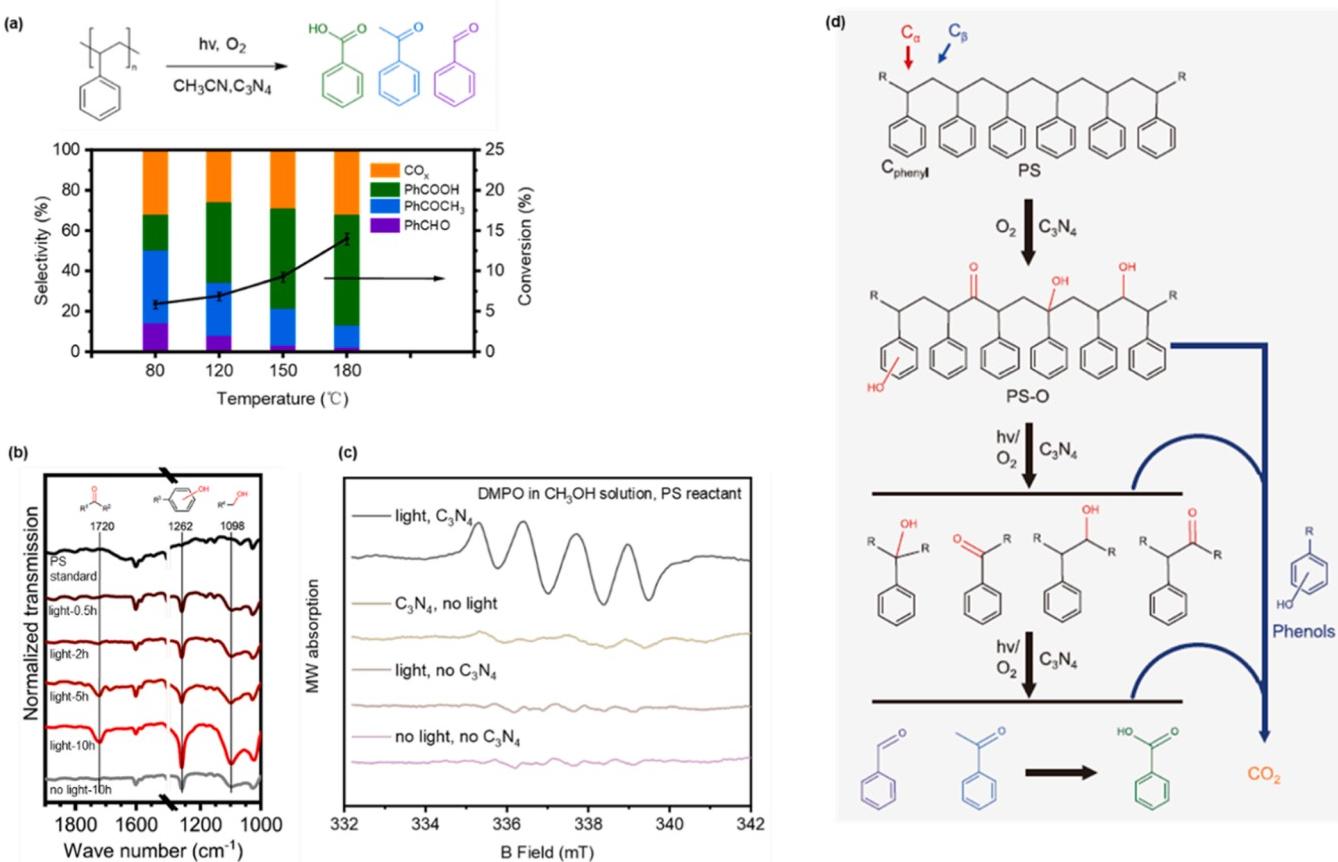


Fig. 4. Thermal-assisted photocatalysis of PS oxidation to produce aromatic oxygenates with $\text{g-C}_3\text{N}_4$ catalyst [37]. (a) Photocatalytic performance of PS oxidation at different temperatures. (b) FTIR spectra of remaining PS after different reaction times. (c) EPR spectra under different conditions. (d) Proposed mechanism of photocatalytic PS oxidation.

concluded that the active species such as $\bullet\text{O}_2$ produced under light irradiation are the key to the fracture of C-C skeleton in PS (Fig. 3d). The thermal effect (high temperature) just improves the solubility of PS in solvent and promotes the mass transfer and diffusion process in the reaction.

In light-driven thermal catalysis, photocatalytic reaction process induced by photogenerated electrons or holes is not involved. The reaction behavior is determined by the thermodynamics at the electronic ground states. The feature of this type of photothermal catalysis is that the catalytic reaction shows similar performance as thermal catalysis when reaction temperature is same. In light-driven thermal system, light is the only energy input for reactions, and the heat required for the reaction is completely generated by the photothermal effect. This way of heating by light has the advantage of generating local hot spots compared to traditional heating. No photogenerated electron-hole pairs are generated or they do not contribute to the reaction during light-driven thermal catalysis. One strategy to verify this can be to introduce electron or hole trapping agents and observe the impact of the trapping agent on the reaction. This strategy is only applicable for non-redox reactions, for the trapping agents usually have redox activity. Another one is to investigate the effects of different wavelengths of light on the reaction separately. Thermal effects are often provided by visible and near-infrared light, while photocatalytic processes (generation of electron-hole pairs) require ultraviolet light with higher energy. Chen and co-workers showed such a system [102] (Fig. 5). They prepare a carbon nanotube modified by polydopamine (CNT-PDA) as light absorber and catalyst to perform PET depolymerization in ethylene glycol. In the comparison of thermal catalysis and photothermal catalysis, the photocatalytic activity has a slight advantage (Fig. 5a).

Theoretical simulation shows that there is local high temperature near the catalyst (Fig. 5b), which can explain the advantage of photothermal catalysis for thermal catalysis at the same apparent temperature. High temperature was conducive to the liquid phase alcoholysis of PET, and the maximum temperature of the reaction was limited by the boiling point of the solvent glycol. By using CNT-PDA as light absorber to heat the solution under solar irradiation, local heating of the absorber led to a high temperature zone in a small range ($< 1 \mu\text{m}$). The existence of these small high temperature zones can improve the catalytic conversion activity of PET on the surface of the catalyst, and ensures that the overall temperature of the solvent will not exceed the limit. The thermal effect in sunlight mainly comes from the visible light part, and most photocatalytic processes require ultraviolet light with higher energy to excite the catalyst or substrate. In order to confirm that the reaction is dominated by thermal effect without photocatalytic process, effect of UV light was investigated (Fig. 5c). No matter whether the catalyst exists or not, ultraviolet light has little effect on the reaction performance. In addition, the nearly equal activation energies of thermal catalysis and photothermal catalysis also indicate that they follow the same reaction mechanism (Fig. 5d).

Photothermal synergistic catalysis includes both photocatalytic pathway and thermal catalytic pathway. The synergistic effect of the two pathways gives the result that is far more different from either of the single pathways. Zeng and co-workers designed Ni-Al-Ti catalysts for the solar pyrolysis of waste plastics [103]. They showed that the photo-generated holes on TiO_2 enabled the fracture of C-C bonds in the large fragment of PE to produce small molecule hydrocarbons, while the thermal catalytic process on Ni improved the selectivity of hydrogen, aromatics and jet fuels in the product. However, the detailed catalytic

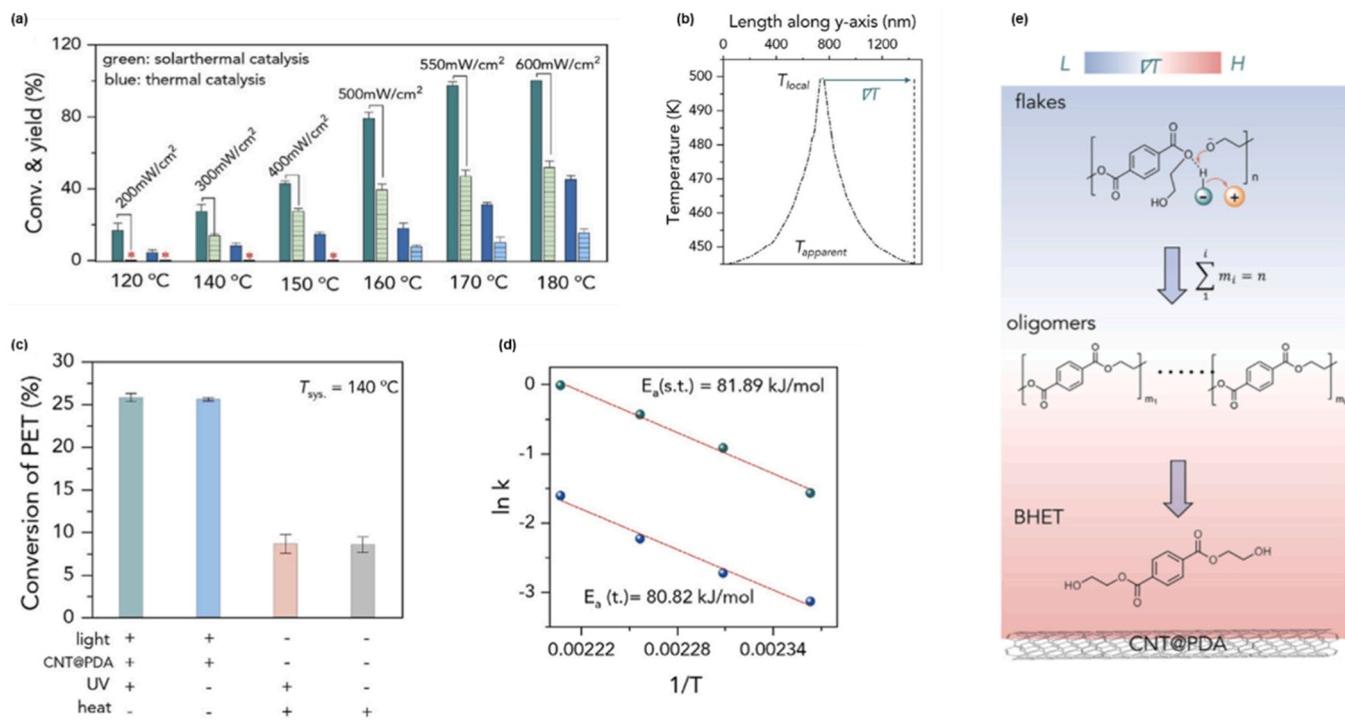


Fig. 5. Light-driven thermal catalysis of PET glycolysis with CNT-PDA catalyst [102]. (a) Effect of solar power/temperature on the conversion of PET and yield of BHET in solar thermal and thermal catalysis. (b) Temperature profile result by line scan in simulated temperature gradient field around one CNT-PDA. (c) Effect of UV light in solar thermal catalysis and thermal catalysis on the depolymerization of PET. (d) Reaction mechanism of glycolysis of PET and temperature gradient by solar thermal catalysts.

mechanism remained unclear in this complex system. Another example of photothermal synergistic catalysis is recently reported by Zhang et al. about the photothermal pyrolysis of HDPE using Ru/TiO₂ catalyst (Fig. 6a) [104]. Ru/TiO₂ catalyst exhibits certain catalytic activity for hydrocracking under thermal catalytic conditions, as ruthenium is a common catalyst for thermal catalytic hydrogenation. The authors find excellent photothermal catalytic performances of Ru/TiO₂ catalyst compared with thermal catalysis (Fig. 6b). The temperature of catalytic hydrocracking can be completely provided by light irradiation. In order to further study the mechanism of photothermal catalysis, the effects of different light on the reaction were investigated under the condition of external heat source (300 °C, Fig. 6c). It was found that UV light had the greatest promoting effect on the reaction. However, the authors exclude the possibility of localized surface plasmon resonance (LSPR) by finite-difference time-domain simulations. It is supposed that UV is directly involved in the activation of C-C bond in PE molecule, and disappearance of crystalline phase in PE under UV irradiation was observed (Fig. 6d). Therefore, the mechanism of this photothermal synergistic catalysis is proposed that the inert polymer chains are first activated by UV light in the incident light, and the visible and near-infrared light parts heat the system to high temperature through photothermal transform to ensure the progress of thermal catalytic C-C deconstruction process on Ru catalyst (Fig. 6e).

Compared with traditional photocatalysis, photothermal catalysis is more effective for some reactions, such as the activation of chemical bonds with high chemical stability. Because photothermal catalysis is more comprehensive in the use of light energy, the economy of photothermal catalysis is more advantageous than that of photocatalysis. However, due to the introduction of strong thermal effect, it may be more difficult to control the product selectivity in photothermal catalysis than in photocatalysis. For the reactions where the product selectivity is important, the application of photothermal catalysis should be cautious. We anticipate that photothermal catalysis will have increasing applications for plastics recycling and upcycling in the future.

3. Future of photocatalysis for plastic recycling and upcycling

3.1. Design and development of new photocatalysis system

Although the photocatalysis for recycling or upcycling plastics has more attractive advantages over traditional thermal catalysis, such as low energy consumption and high selectivity to special product, the efficiency is too low for practical applications. Besides, plastics may only be activated by the oxidative half reactions of photocatalysis. The very active photocatalytic system may over-oxidize plastics to CO₂ and H₂O, and the moderate ones may not activate plastics. Thus, seeking highly active photocatalysts alone for plastics upcycling may not be an ideal solution. Developing multifunctional photocatalytic systems that can activate plastics into active radicals and then convert these radicals to valuable products is a potential solution.

The photothermal catalysis that includes the synergy of photocatalysis and thermal catalysis exhibits high potential for plastics upcycling. It can provide photons to initialize the reaction and thermal energy to overcome the energy barrier of reaction. The thermal energy may also promote the transmission of photo-generated charge carriers. So, some photothermal catalysis for plastics upcycling could proceed smoothly with high efficiency. Ideally, all the thermal energy for photothermal catalysis should come from the light irradiation during a reaction. Therefore, the key for photothermal catalysis is to design a catalyst that can absorb light and convert photo energy to thermal energy. The black catalysts composed of semiconductor support and active transition metals may function as excellent photothermal catalysts for the upcycling of plastics. In addition, the carbon encapsulation of active transition metal can also improve the light absorption ability and promote the electron transmission during the photothermal process. To improve the temperature around catalyst, a convex glass can be equipped on the top of the reactor to focus natural light on the surface of catalyst. As expected, the photothermal catalysis involving the photons absorption and thermal electron transfer can bring complexity on the

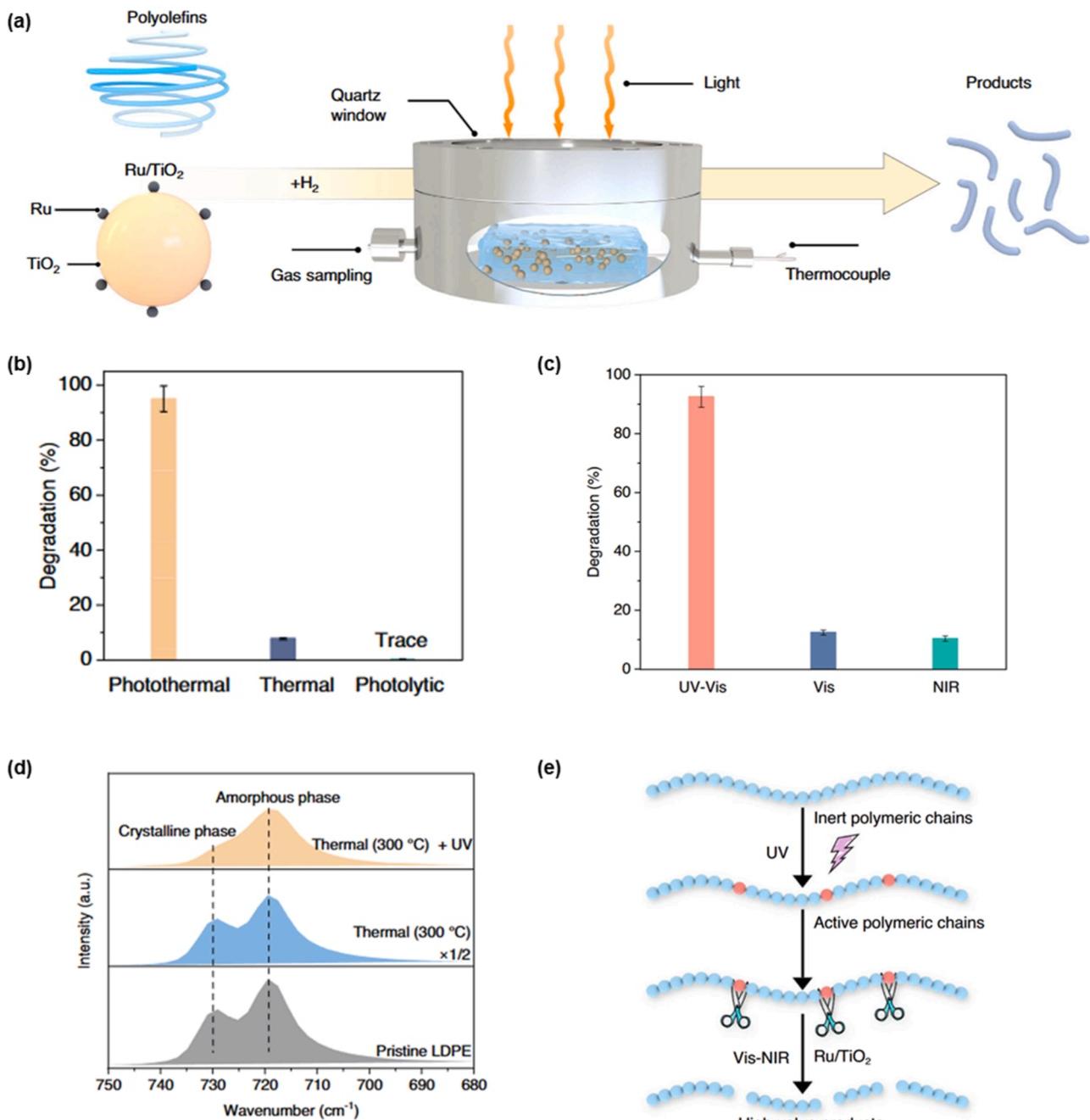


Fig. 6. Photothermal synergistic catalysis for PE hydrocracking using Ru/TiO₂ catalyst [104]. (a) Schematic illustration of the photothermal polyolefin plastic recycling system. (b) Degradation percentages of LDPE under various reaction conditions for 20 h (300 °C for photothermal and thermal experiment, room temperature for photolytic experiment). (c) Temperature profiles of the ambient-pressure reactor, LDPE, Ru/TiO₂, and mixture under illumination from a Xe lamp at the same light intensity. (d) Degradation of LDPE over Ru/TiO₂ under different irradiation. (e) Pro-posed photothermal reaction mechanism.

catalytic mechanism.

3.2. Utilizing sunlight instead of artificial light sources

Artificial light source, such as the xenon lamp, is usually the light source of photocatalysis or photothermal catalysis for plastic upcycling in laboratory, which has higher intensity than natural solar irradiation. The efficiency of these artificial light sources in converting electrical energy input into light energy is usually low. In order to make the procedure of recycling or upcycling plastics green and sustainable, the photocatalysis or photothermal catalysis under solar irradiation should be evaluated. To reach the light intensity of xenon lamp, a convex glass

or collector mirror should be adopted.

To utilize the solar energy extensively in plastics upcycling, another procedure called the photo-induced thermal catalysis (with no photocatalysis or photothermal catalysis) can be considered. By the effect of photo-induced heating, the thermal energy from solar irradiation has been used widely to cook food or heat water in our daily life. The highest temperature in a vacuum photothermal transform tube equipped on a collecting mirror under solar irradiation can reach above 450 °C, which can promote most of plastic upcycling procedures such as pyrolysis and hydrogenolysis. Therefore, by designing a suitable reactor, the traditional thermal catalysis reaction for plastic upcycling can be conducted under natural solar irradiation successfully. This strategy avoids the

design of catalyst possessing photocatalytic activity and uses simple thermal catalytic process. The catalytic mechanism can be seen as same as the thermal catalysis.

3.3. Consideration of practical application in plastic recycling

More than the fundamental research involved, chemical recycling of plastic waste is a practical field. It will need extra efforts to explore the practicability and robustness of laboratory methods for plastics recycling. For example, even if a catalytic system works with high efficiency, reasonable mass balance, large turnover number (TON) in the lab, applying such a catalytic system to real-life plastics will be subject to the influence of contaminants and impurities. Furthermore, plastics recycling should meet the following requirements prior to the scale-up implementations. The use of stoichiometric chemical reagents, excessive organic solvent, and expensive noble metal catalysts should be avoided.

Another challenge in plastic recycling is that waste plastics are typically mixtures of multiple types of polymers, with other possible additives and contaminants, while most of the plastics recycled in the published research are pure or single type polymer. Although some reported catalytic systems are claimed to be applicable for multiple types of polymers, few has conducted the chemical recycling or upcycling of mixed plastics. It would be intriguing to convert a variety of mixed plastics into a single product or a class of products by a single step, or convert different types of plastics hierarchically by multiple independent chemical steps from mixed plastic waste.

CRediT authorship contribution statement

Ruochen Cao: Writing – original draft, Writing – review & editing, Visualization, Investigation, Formal analysis. **Dequan Xiao:** Writing – review & editing. **Meng Wang:** Conceptualization, Supervision, Visualization. **Yongjun Gao:** Writing – original draft, Writing – review & editing, Supervision, Visualization. **Ding Ma:** Writing – review & editing, Conceptualization, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123357](https://doi.org/10.1016/j.apcatb.2023.123357).

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